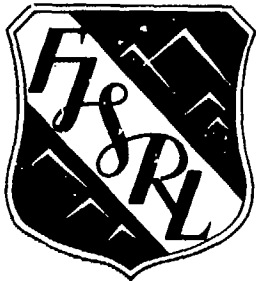


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**FRANK J. SEILER RESEARCH LABORATORY**

**FJSRL TR-81-0011**

**OCTOBER 1981**

**A NEW CLASS OF ROOM  
TEMPERATURE MOLTEN SALTS  
FOR BATTERY APPLICATIONS**

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**PROJECT 2303**

**AIR FORCE SYSTEMS COMMAND**

**UNITED STATES AIR FORCE**

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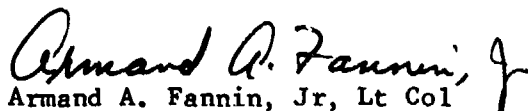
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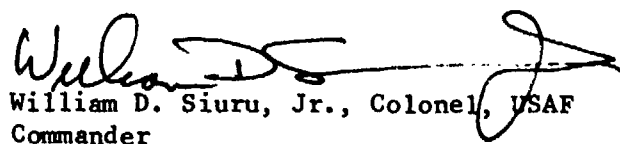
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2

A NEW CLASS OF ROOM TEMPERATURE  
MOLTEN SALTS FOR BATTERY APPLICATION

By

Dr. John S. Wilkes  
Maj Joseph A. Levisky  
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Directorate of Chemical Sciences  
The Frank J. Seiler Research Laboratory  
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# TABLE OF CONTENTS

Summary. . . . .	ii
Preface. . . . .	iii
Illustrations. . . . .	iv
Table 1, Conductivities. . . . .	iv
Introduction . . . . .	1
Objective. . . . .	3
Results and Discussions. . . . .	4
Conclusions. . . . .	10
References . . . . .	11
Table 1. . . . .	12
Figure Legends . . . . .	13
Abbreviations and Acronyms . . . . .	24

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## SUMMARY

Salts that are liquid at room temperature would provide a completely ionic electrolyte for rechargeable batteries without the penalty of high operating temperatures. We have discovered and characterized a new class of molten salts that are liquids considerably below room temperature. The new materials are mixtures of dialkylimidazolium chlorides and aluminum chloride. The solid-liquid phase diagram of one member of the class shows that the material is liquid below room temperature over its entire composition range. A proof of concept battery cell using the new electrolyte was demonstrated. Electrochemical tests show that battery anodes and cathodes will operate in the new electrolytes. By varying the ratio of the components of the new melts, the chemical and physical properties can be changed over a very wide range.

## PREFACE

The research described here was presented at the 1981 AFSC/NAVMAT Science and Engineering Symposium, 27-29 October 1981 at Wright-Patterson AFB, OH. Part of the work was done as a reserve project by Maj Levisky and Capt Hussey.



## ILLUSTRATIONS

	PAGE
Figures 1, Electrical Conductivities . . . . .	14
Figure 2, Crystalline and Molten Lithium Chloride. . . . .	15
Figure 3, Molten and Dissolved Lithium Chloride. . . . .	16
Figure 4, Operating Temperatures . . . . .	17
Figure 5, LUMO Energies. . . . .	18
Figure 6, Phase Diagram. . . . .	19
Figure 7, Cyclic Voltammogram. . . . .	20
Figure 8, Densities. . . . .	21
Figure 9, Battery Cell . . . . .	22
Figure 10, Discharge Curve . . . . .	23

## TABLE

Table 1, Conductivities . . . . .	12
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## INTRODUCTION

Electrical power sources are required for almost all modern transportation, communication and weapon systems. For many of these systems the power can be best supplied by batteries of various kinds. A partial list of battery needs for military applications includes detection (guided projectiles, sonobouys, surveillance devices, etc.), fuzing (bombs, mines, torpedos, etc.), propulsion (submarines, swimmer delivery vehicles, ground transport, etc.), guidance and control (radar, laser designators, satellites, etc.) and communications (radios, display systems). The Air Force has specific battery applications for aircraft, survival equipment, munitions, missiles and remotely piloted vehicles. Many military battery requirements can be met by existing batteries developed for consumer or industrial applications, but often unusual electrical requirements or severe operating environments require the development of unique batteries for the military. Some basic research in these advanced batteries is the subject of this paper.

All batteries consist of a minimum of three components: the anode, the cathode and the electrolyte. The anode and cathode are the locations where the chemical reactions occur that generate an electrical current, and they largely determine the voltage and capacity of the battery cell. The electrolyte provides an electrically conductive medium for the chemical reactions, and largely determines the resistance of the battery cell as well as sets limits on the operating environment for the cell (temperature, pressure and g-forces). Most

familiar batteries use water-based (aqueous) electrolytes, with dissolved salts to provide electrical conductivity. Some more advanced batteries have employed non-aqueous organic or inorganic liquids as the electrolyte, again with dissolved salts added to provide conductivity. A few batteries have used a solid salt electrolyte, such as  $\text{RbAg}_4\text{I}_5$ , which has a very low conductivity but wide operating temperature range. Conductivity of an electrolyte is an important physical property with respect to battery applications, since it is often electrolyte conductivity that determines the internal resistance of a battery, and thus the maximum current that this battery can provide. Figure 1 compares the conductivities of the various types of electrolytes that are employed in batteries<sup>1</sup>. It is clear that if conductivity were the sole criterion for electrolyte selection, molten salts would be the first choice.

Molten salts are pure ionic liquids, and therefore do not need the addition of salts to provide conductivity. When in the crystalline state, salts are also ionic, but are immobile and usually non-conductive. Upon melting "holes" open up in the structure and the ions become mobile, allowing ionic conduction, as shown in Figure 2<sup>2</sup>. Molten salts are more conductive than aqueous and non-aqueous salt solutions because the ions are present in higher concentration and are not solvated. Figure 3 compares these two types of electrolytes. Of course the reason that few batteries use molten salts as the electrolyte is that most salts are liquid only at very high temperatures. Figure 4 compares the operating temperatures of different

types of electrolytes<sup>1</sup> and it is clear that conventional molten salts operate at such high temperatures that there would be some obvious incompatibilities with common battery construction materials and with system components (e.g., electronics) nearby.

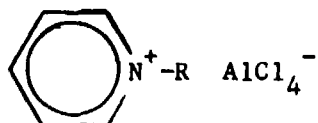
In this laboratory there has been a long-term interest in developing lower melting fused salt electrolytes for battery applications<sup>2</sup>. Mixtures of sodium chloride and aluminum chloride were successfully used as the electrolyte in a thermal battery, but the minimum operating temperature was over 175°C. In order to achieve lower operating temperatures we investigated mixtures of 1-alkylpyridinium chlorides and aluminum chloride, some of which are molten at room temperature. Studies of the physical properties<sup>3</sup> of these melts and the electrochemistry of metal ions dissolved in them<sup>4-7</sup> indicated that they have some promise as battery electrolytes. In this paper we describe some new molten salts that are true ionic liquids (i.e., molten salts) at room temperature and below. We report some physical and chemical properties of the new molten salt that are important in battery applications and we demonstrate a battery cell using the new material as the electrolyte.

#### OBJECTIVE

The goal of current electrolyte research at this laboratory is the development of low melting molten salts suitable for batteries. In order to achieve this goal new materials must be synthesized, their chemical and physical properties determined and battery cells using the new electrolytes demonstrated.

## RESULTS AND DISCUSSION

As stated earlier, we have already evaluated one class of low melting molten salts: the mixtures of 1-alkylpyridinium chlorides with aluminum chlorides. One deficiency of these melts is that the

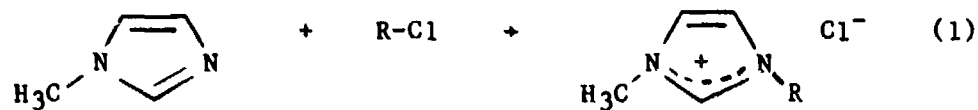


### alkylpyridinium chloroaluminate

electrochemical window is foreshortened at the cathodic end. The electrochemical window is the difference between the anodic and cathodic decomposition potentials, and ultimately limits the voltage that a battery cell could provide. We determined by electron paramagnetic resonance experiments<sup>6</sup> that the problem was due to reduction of the alkylpyridinium cation, which occurs at a potential more positive than Al(III) in the melts. With this knowledge we embarked on a research program to find an organic chloride salt that would not be readily reduced in the melt, but would still form a low melting material when mixed with aluminum chloride.

One might expect that any large organic cation could produce chloroaluminates that are molten at or near room temperature. The most common source of positive charge in organic compounds is a quaternary nitrogen, as in the alkylpyridinium cations described

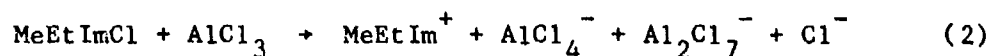
above. For these reasons we focused our search on large (molecular weight more than 130) molecules containing quaternary nitrogen. While many such organic cations probably would be large enough, the cations must also have reduction potentials more negative than Al(III) in the melts in order to be unreactive towards Al and to improve the electrochemical window. Using Dewar's MNDO molecular orbital calculation technique<sup>9</sup>, we calculated the energies of a variety of organic cations as a screen for species that would be less easily reduced than 1-alkylpyridinium ions. Figure 5 shows the results of some of those calculations. LUMO energy is the energy of the lowest unoccupied molecular orbital in a molecule, and is a value that may be correlated with reduction potentials. Each electron volt change in LUMO energy should correspond to an equivalent change in the voltage at which the molecule is reduced in solution. Of the five types of compounds shown in Figure 5, one type (I) should be more easily reduced than the alkylpyridiniums (II) and three (types III, IV and V) should be less easily reduced. The 1,3-dialkylimidazolium salts (type IV) were revealed as attractive candidates, since their reduction potentials were predicted to be about 0.8 V lower than the 1-alkylpyridinium salts, and they could be prepared readily from commercially available starting materials. A series of 1,3-dialkylimidazolium chlorides were prepared using a strategy similar to that employed for the synthesis of the iodide salts<sup>10</sup>, as shown in equation 1.



R = methyl, ethyl, propyl, butyl or benzyl

The compound where R is an ethyl substituent was particularly easy to prepare and, as was later determined, formed chloroaluminate melts with very desirable properties. For these reasons that compound, 1-methyl-3-ethylimidazolium chloride (MeEtImCl), was selected for further study and evaluation.

The chloroaluminate melt was prepared by simply mixing aluminum chloride with the MeEtImCl, as in equation 2. The two white solids



combined to produce a clear, slightly viscous liquid. The anionic species shown on the right hand side of equation 2 are all present in the chloroaluminate melt, but their relative proportions depend on the ratio of  $\text{AlCl}_3$  to MeEtImCl used in the preparation. All operations involving aluminum chloride or chloroaluminate melts were done in a glove box containing a dry argon atmosphere.

The physical, chemical and electrochemical properties of a new melt must be determined to evaluate its merit as a potential battery electrolyte. Such features as solid-liquid phase equilibria (melting behavior), electrochemical window, conductivities, viscosities,

densities, acid-base properties and melt structure require study. Since the imidazolium chloroaluminate melts are completely new materials, all of the studies must be done, and in some cases new techniques must be developed.

Since the major aim of the project is to obtain molten salts that are liquid under ambient conditions, the temperature range where the MeEtIm melt is molten is of primary importance. Information of this type is embodied in the phase diagram for the melt. Previously published work in the alkali halide chloroaluminate melts<sup>11</sup> showed that the melting points of such mixtures are dependent on the relative proportions of the alkali halide (e.g., NaCl) and  $\text{AlCl}_3$ . Although we have not completed the entire phase diagram for the MeEtIm chloroaluminate system, we have characterized the single phase region between 0.3 and 0.7 mole fraction  $\text{AlCl}_3$ , as shown in Figure 6. Note that over the entire composition range studied the solid-liquid line lies below room temperature, and in some places is almost as low as  $-100^\circ\text{C}$ . The very low melting sections of the phase diagram are probably glass transitions, which are unusual in molten salts. All attempts to induce true crystallization in those regions have been unsuccessful to date. Above 0.67 and below 0.32 mole fraction  $\text{AlCl}_3$ , solid and liquid phases coexist, thus compositions in those regions are probably not useful as electrolytes. The low melting temperatures for the new MeEtIm chloroaluminate molten salt are the lowest ever observed for true molten salts.



As stated earlier, the width of the electrochemical window for an electrolyte is an important parameter. The window of the new MeEtIm chloroaluminate melt was determined by cyclic voltammetry, as shown in Figure 7. The cyclic voltammogram shows an anodic limit at above +1.8 V vs an aluminum reference, which is the chloride oxidation observed in all chloroaluminate melts at about that potential. Unlike other chloroaluminates, the cathodic limit is extraordinarily low; about -1.3 V. This results in an electrochemical window of about 3.1 V, and is due the low reduction potential of the imidazolium cation. The magnitude of the window implies that batteries having voltages of over 3 volts per cell could be constructed.

In general chloroaluminate melts exhibit interesting acid-base chemistry governed by the equilibrium in equation 3.



The value of the equilibrium constant for equation 3 determines the range of chloride ion concentration available, which in turn greatly affects the chemical behavior of the melt. The new MeEtIm chloroaluminate melt was titrated using previously described techniques<sup>12</sup>, and the equilibrium constant was found to be  $2.0 \times 10^{-19}$  for equation 3. This value is the lowest yet reported for any chloroaluminate, and implies that a wider range of chloride ion concentrations are attainable in the new melt compared to all others.

Densities, viscosities and electrical conductivities as functions of melt composition and temperature are necessary in order to make practical use of the new melt. Of these only the density experiments have been completed in detail. Figure 8 shows a family of density vs composition curves for temperatures ranging from 20°C to 80°C. For each temperature the density is a quadratic function of  $\text{AlCl}_3$  mole fraction, as commonly seen in other molten salts. The density data will be useful in later studies of the physical properties of the new melt. The conductivities of some compositions of the 1-methyl-3-ethylimidazolium melt are tabulated in Table 1. They are not very high by molten salt standards, but this is probably largely due to the temperature at which they were measured. The values are approximately the same as for the 1-alkylpyridinium chloroaluminate melts<sup>5</sup>.

In order to design a battery cell properly, more electrochemical experiments must be performed on potential cathodes (depolarizers) and anodes in the new melt. Nevertheless, we constructed a prototype battery cell, using an aluminum anode and iron(III) chloride cathode. The construction of the cell is shown in Figure 9. The anode is simply a disk of aluminum separated from the cathode compartment by a fine porosity glass frit. The construction of the cathode takes advantage of an interesting chemical feature of the new melt. Benzene is soluble in the melt, but causes the  $\text{FeCl}_3$  to become insoluble. Thus we were able to construct an insoluble cathode, which is in electrical contact with a tungsten current collector. Figure 10 shows

a discharge curve at constant current for the cell. This is clearly not an optimum design, either chemically or mechanically, but two items are noteworthy. First, the discharge is quite flat, dropping off sharply when the Fe(III) is depleted. Second, this is the first true molten salt battery that operates as low as 20°C. The cell constitutes a proof-of-concept, and is an important milestone in our effort to develop an ambient temperature rechargeable molten salt battery. Experiments are in progress to find better redox couples for battery electrodes and to design a cell that will provide meaningful battery performance data.

#### CONCLUSIONS

We have prepared, characterized and partially evaluated a new molten salt that has great potential for battery applications. It is liquid in a temperature range of about -100°C to over +150°C, which includes most operating environments for military systems. Its electrochemical window is over 3 volts, which would allow the construction of 3 volt battery cells. Further development of this new electrolyte could provide high energy density batteries that could operate over a very wide temperature range.

## References

1. R. Jasinski, High-Energy Batteries, Plenum Press, New York (1967), p 96.
2. H. Bloom, The Chemistry of Molten Salts, W.A. Benjamin, Inc., New York (1967), p 13.
3. R. Jasinski, op. cit., p. 97.
4. J. C. Nardi, J. K. Erbacher, C. L. Hussey and L. A. King, J. Power Sources, 3, 81 (1978).
5. R. A. Carpio, L. A. King, R. E. Lindstrom, J. C. Nardi and C. L. Hussey, J. Electrochem. Soc., 126, 1644 (1979).
6. C. L. Hussey, L. A. King and R. A. Carpio, J. Electrochem. Soc., 126, 1029 (1979).
7. C. L. Hussey, L. A. King and J. S. Wilkes, J. Electroanal. Chem., 102, 321 (1979).
8. J. S. Wilkes, unpublished results.
9. M. Dewar, H. Kollmar and S. Suck, Theoret. Chim. Acta, 36, 237 (1975).
10. J. S. Wilkes and J. A. Levisky, Frank J. Seiler Research Laboratory Technical Report, FJSRL-TR-81-0001, January 1981, ADA 094772.
11. C. R. Boston, in Adv. in Molten Salt Chem., 3, 140 (1971).
12. R. J. Gale and R. A. Osteryoung, Inorganic Chem., 18, 1603 (1979).

TABLE 1

## Conductivities of MeEtIm Chloroaluminate Melts

Molefraction AlCl <sub>3</sub>	Specific Conductivity (ohm-cm)	Temperature (°C)
44	0.0117	29.7
50	0.0227	30.9
67	0.0154	32.2

### Figure Legends

1. Electrical Conductivities of Electrolytes.
2. Ions in Crystalline and Molten Lithium Chloride. Small circles are  $\text{Li}^+$  and large circles are  $\text{Cl}^-$ .
3. Ions in Crystalline and Dissolved Lithium Chloride. Dark circles are  $\text{Li}^+$  and  $\text{Cl}^-$ ; open circles are O and H of water molecules.
4. Operating Temperatures of Electrolytes.
5. Calculated Energies of the Lowest Unoccupied Molecular Orbitals. Calculated for five different types of molecules.
6. Phase Diagram for the MeEtIm Chloroaluminate Salt.
7. Cyclic Voltammogram of a MeEtIm Chloroaluminate Molten Salt. Performed on a 0.42 mole fraction  $\text{AlCl}_3$  melt at 30 °C at a glassy carbon electrode, vs an Al reference electrode. Scanned at 100 mV/sec.
8. Densities of MeEtIm Chloroaluminate Melts.
9. Experimental Battery Cell.
10. Battery Discharge Curve. Obtained from cell shown in figure 9, using an Al anode,  $\text{FeCl}_3$  cathode and a MeEtIm chloroaluminate electrolyte containing 50% (v/v) benzene.

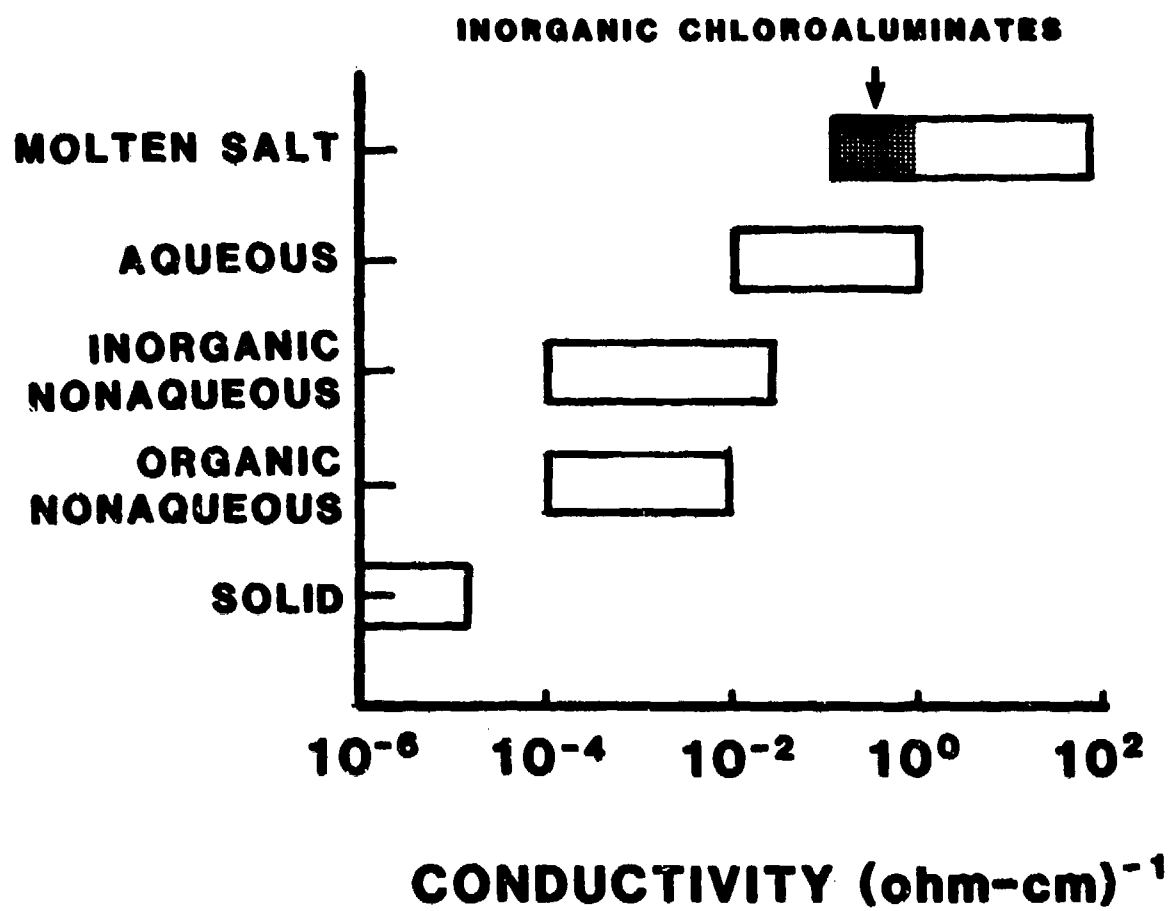
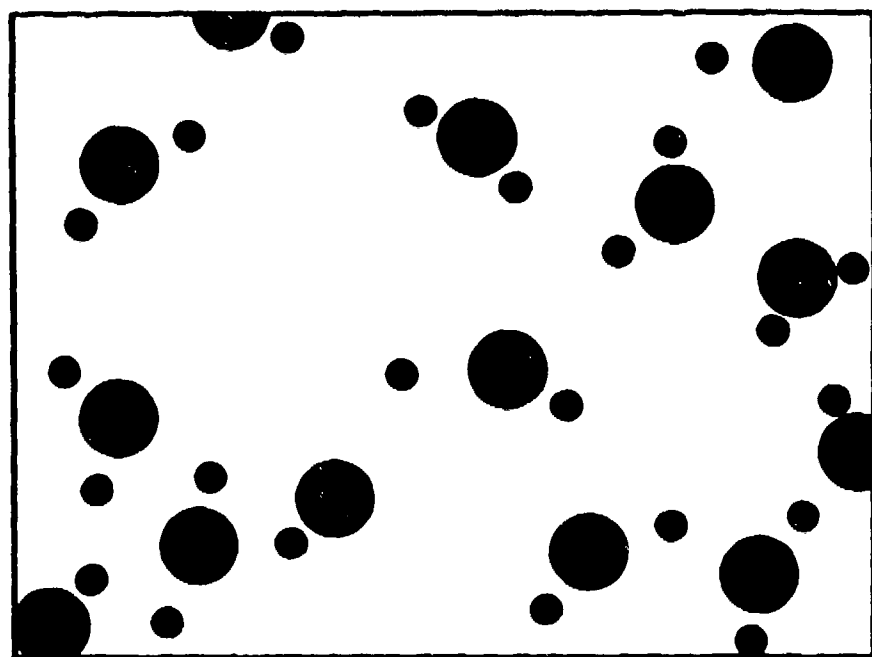
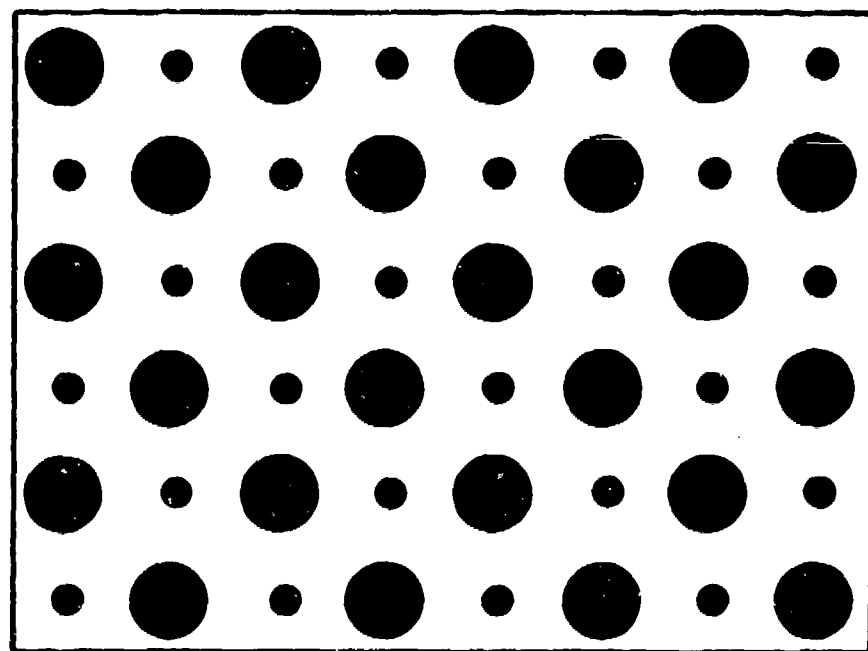


FIGURE 1



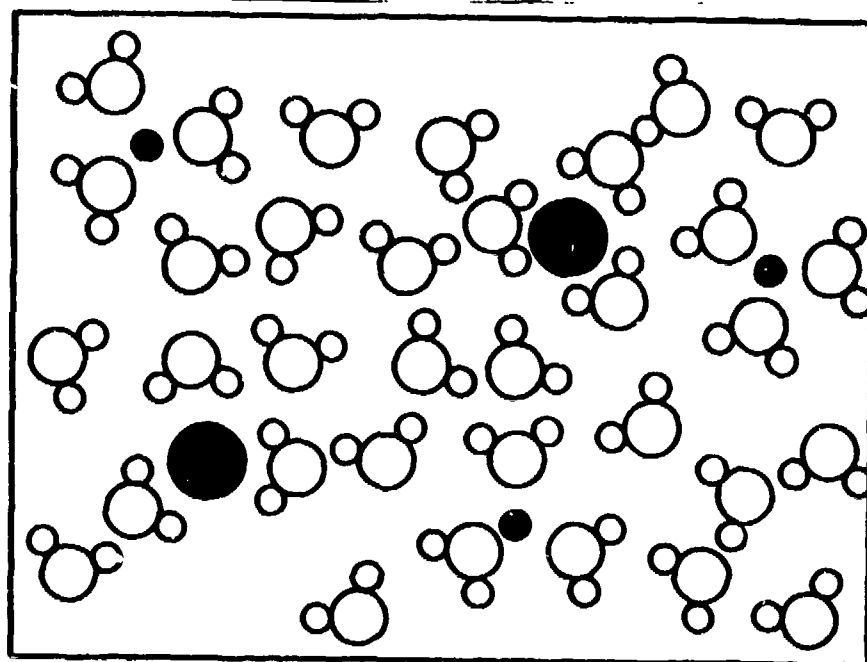
MOLTEN



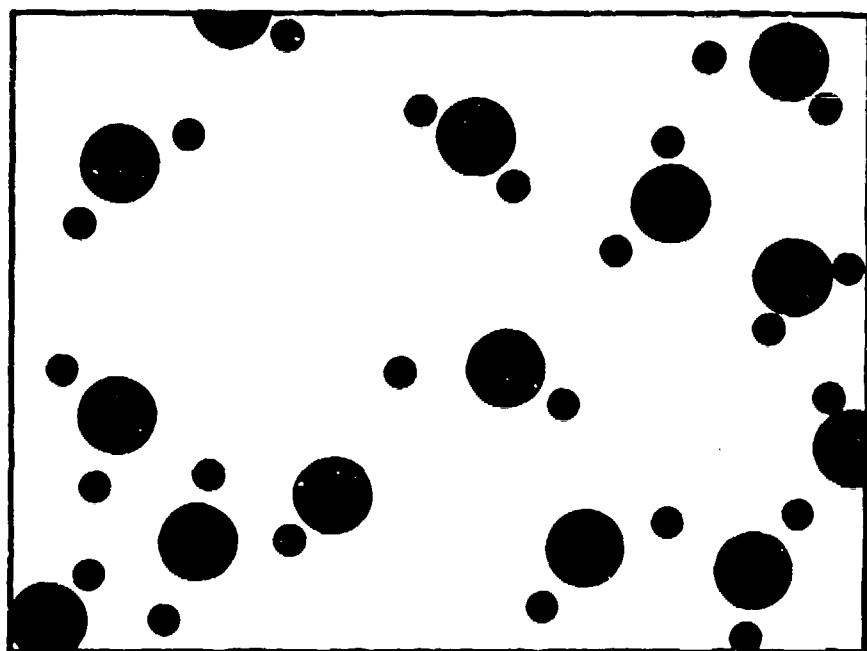
CRYSTAL

FIGURE 2





SOLUTION



MOLTEN

FIGURE 3

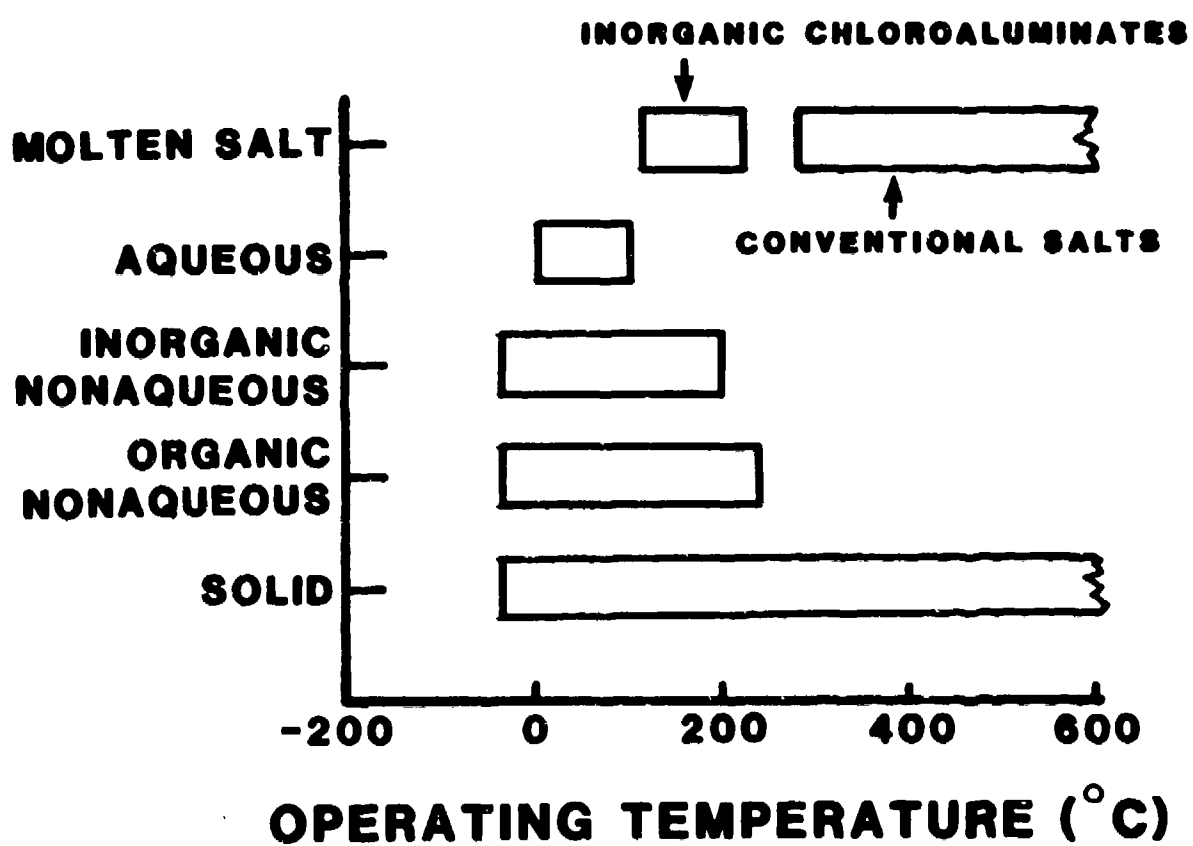


FIGURE 4

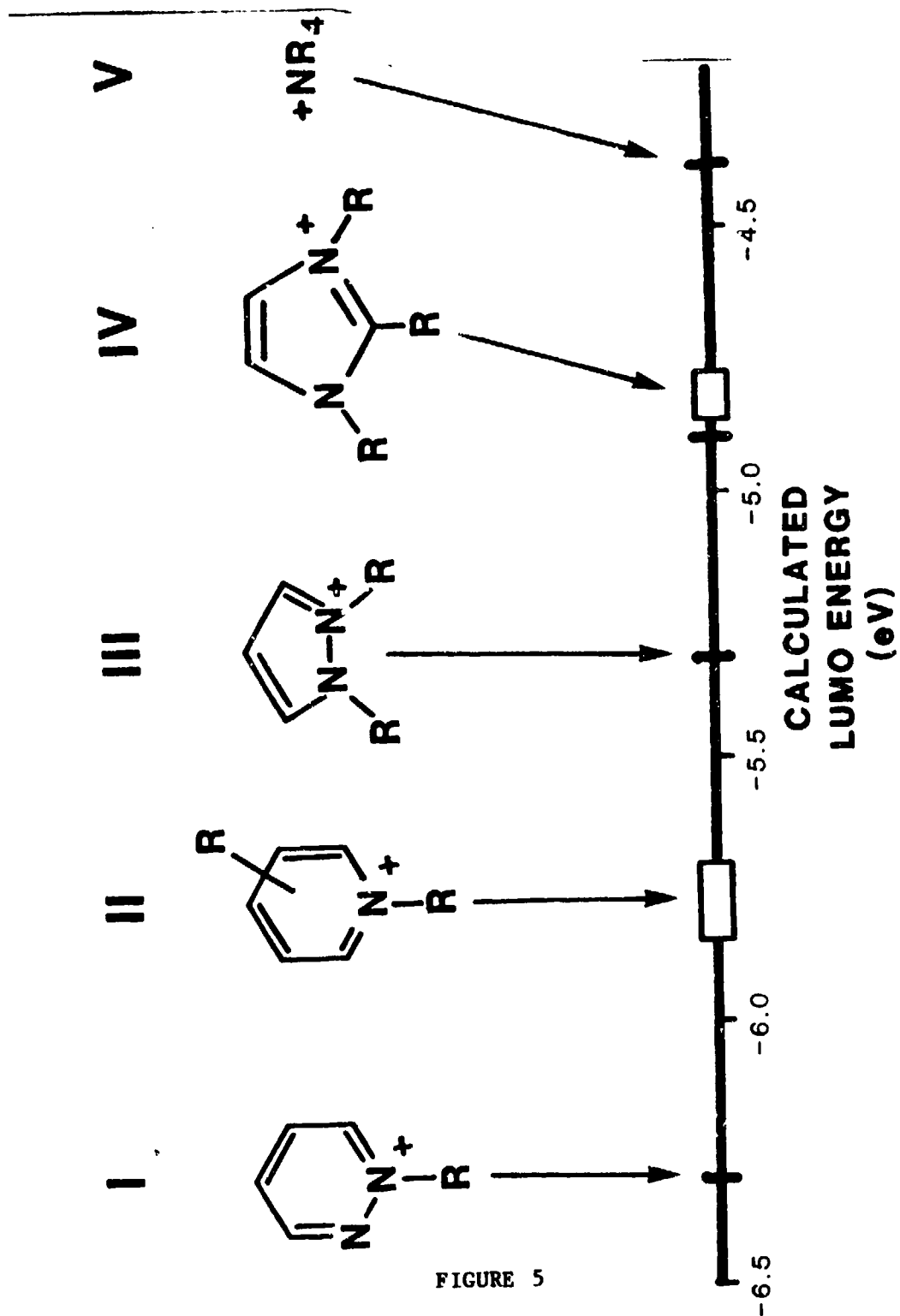


FIGURE 5

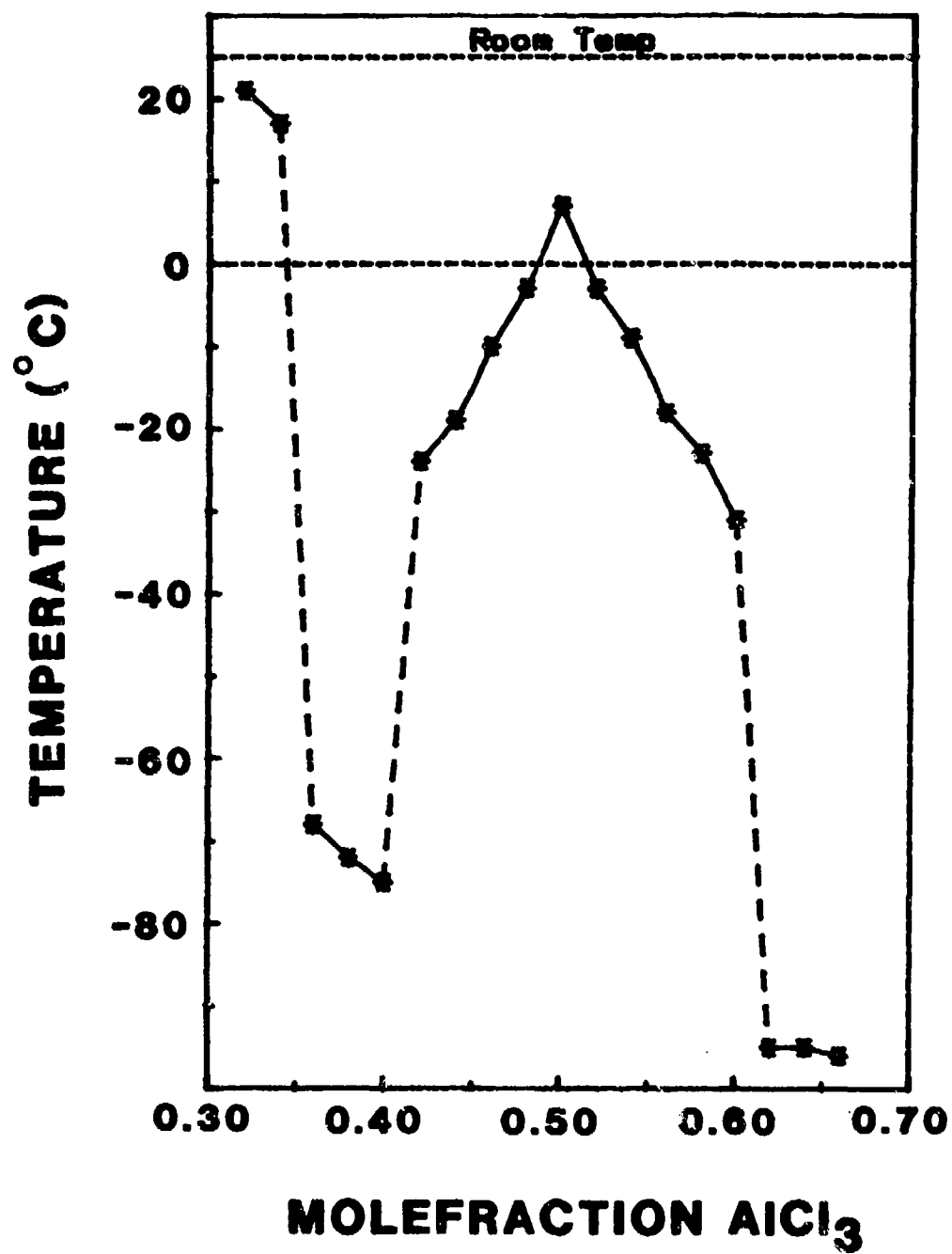


FIGURE 6

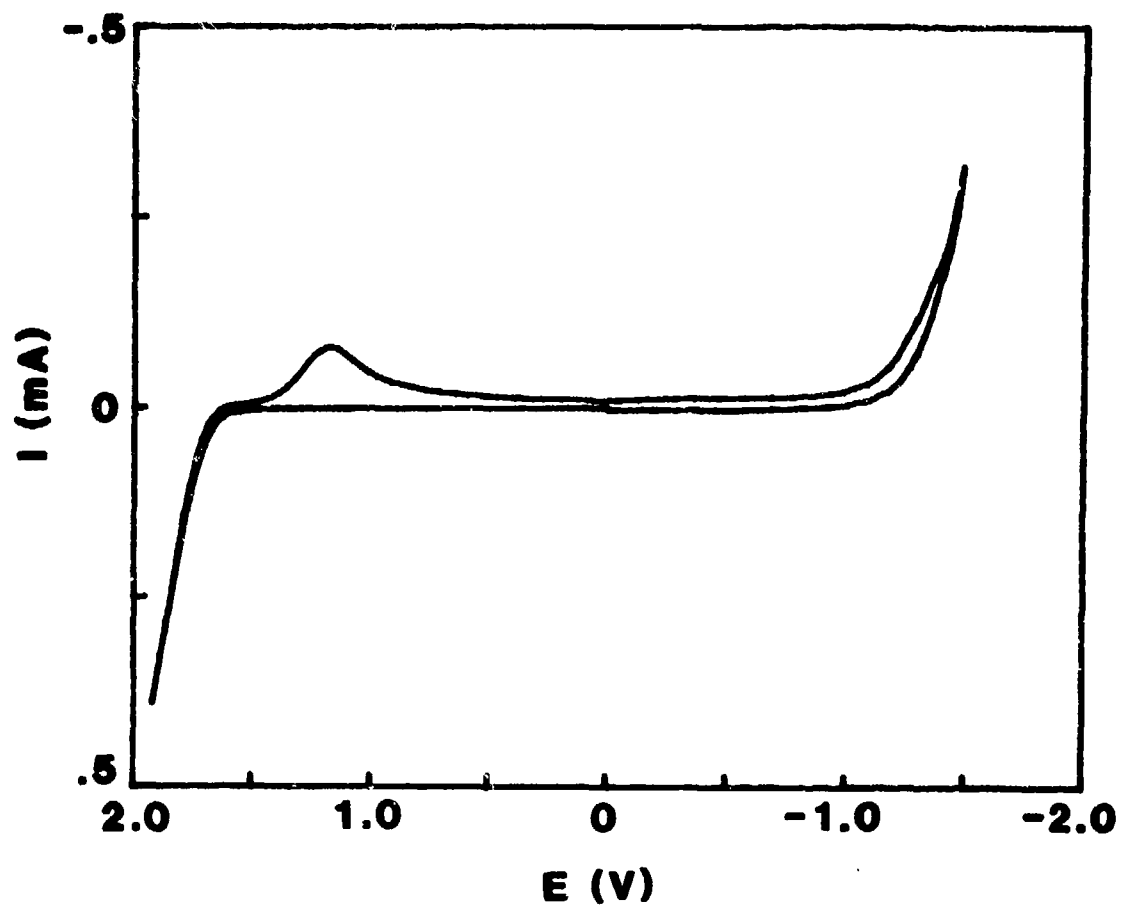


FIGURE 7

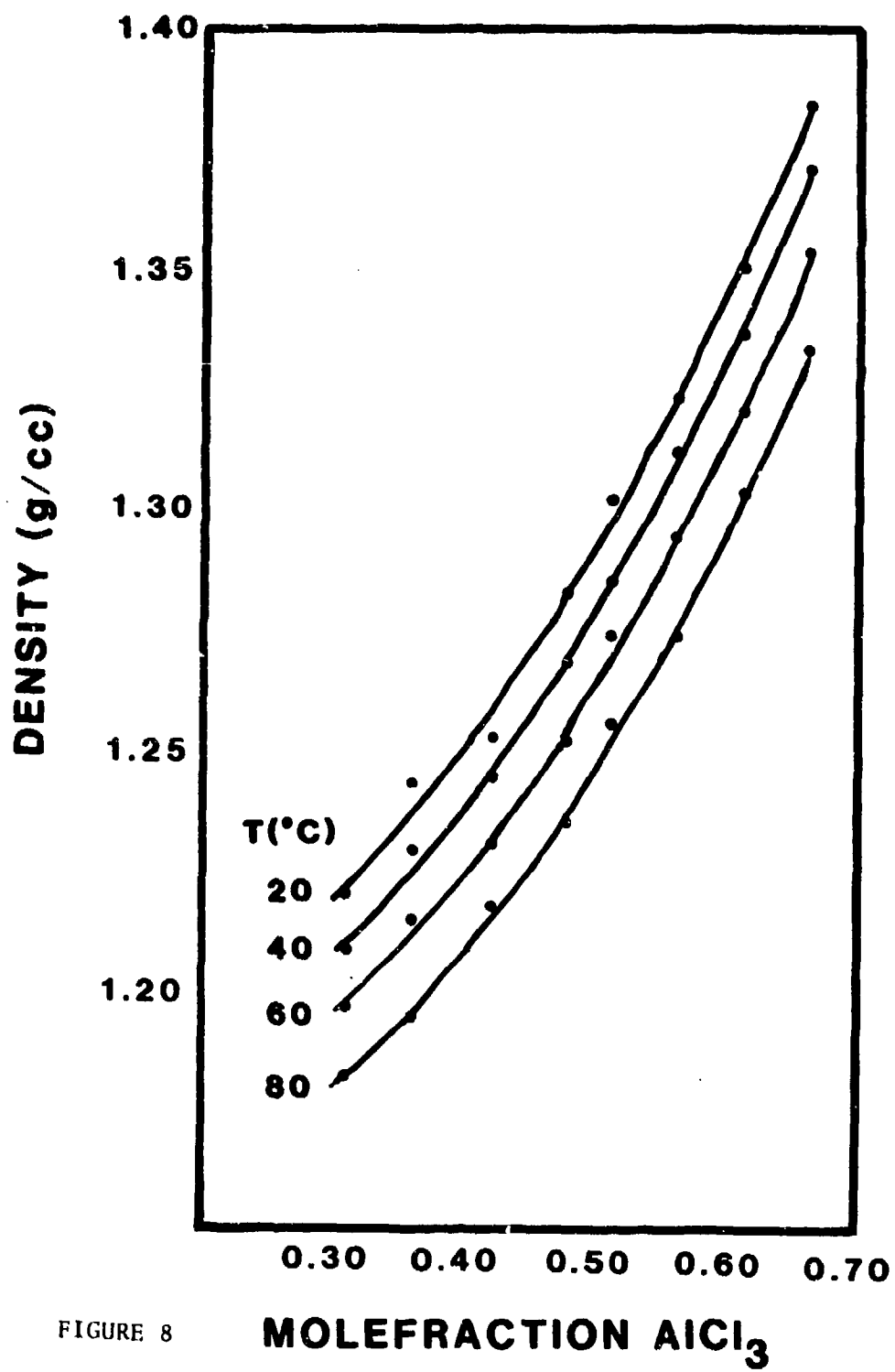
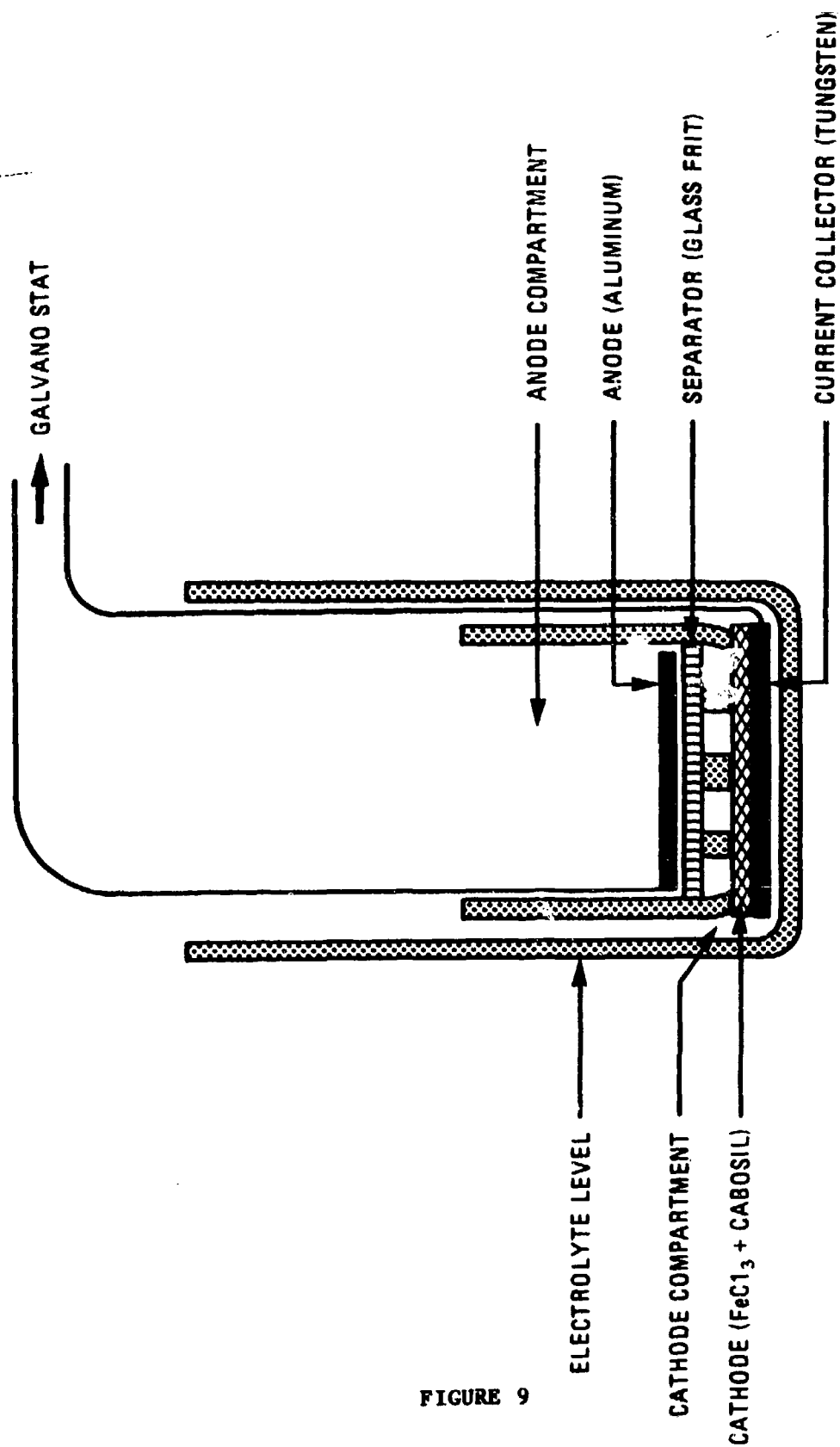


FIGURE 8



SINGLE CELL BATTERY

FIGURE 9

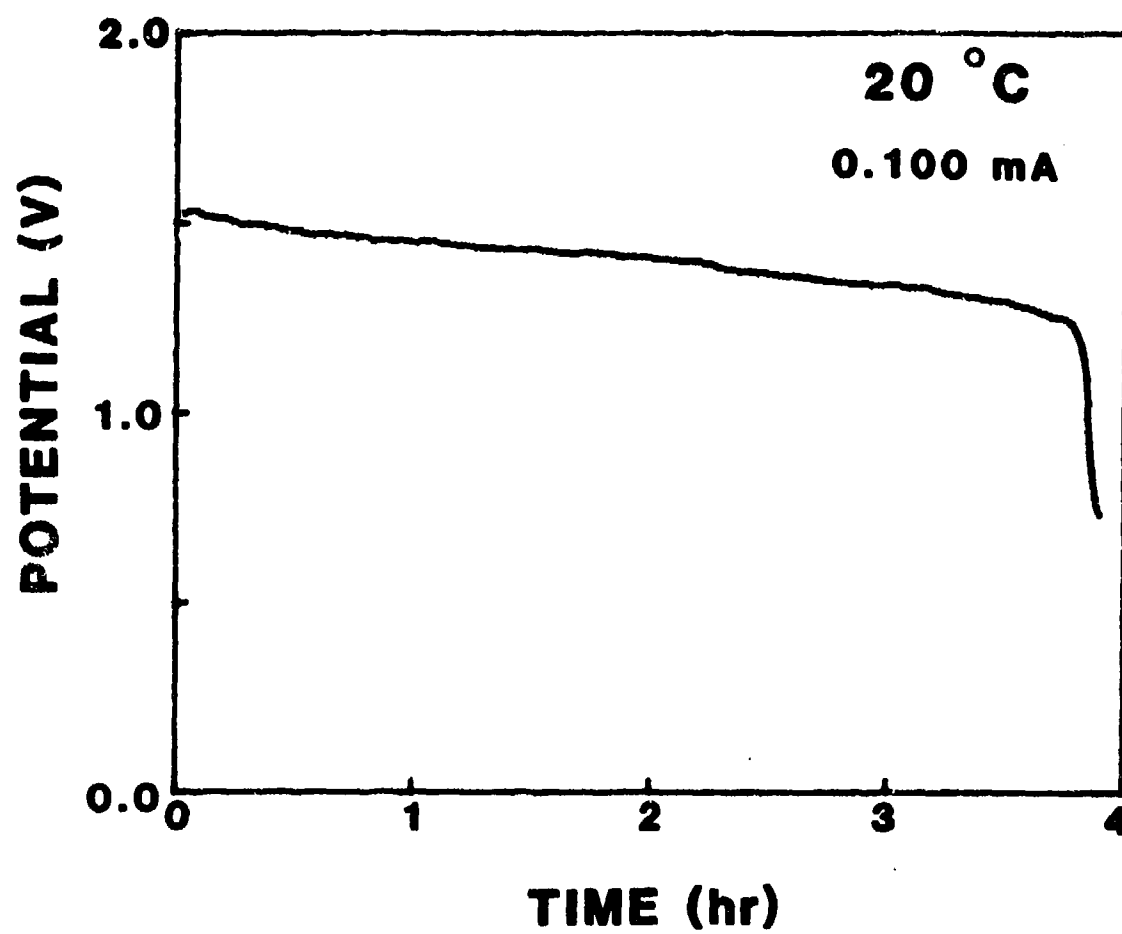


FIGURE 10



# ABBREVIATIONS and ACRONYMS

LUMO . . . . . Lowest unoccupied molecular orbital  
MeEtIm<sup>+</sup> . . . . . 1-methyl-3-ethylimidazolium cation  
MeEtImCl . . . . . 1-methyl-3-ethylimidazolium chloride  
MNDO . . . . . modified neglect of diatomic overlap